

# Mixed radical iodine charge-transfer salts of dithiadiazolyl diradicals. Structural characterization of the pyridine-bridged 2:1 salt 2,6-[(S2N2C)C5H3N(CN2S2)](2)[I]

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**Table S1** Crystal and refinement data for $[P\text{-}2,6\text{-}S]_2[I]$.

| | |
|---|---|
| formula | $IS_8N_{10}C_{14}H_6$ |
| fw | 348.83 |
| crystal size, mm | 0.51 x 0.11 x 0.08 |
| crystal color | black |
| crystal mount | on glass fiber by epoxy |
| *a*, Å | 3.434(3) |
| *b*, Å | 9.8914(9) |
| *c*, Å | 30.803(4) |
| $\beta$, deg | 91.52(3) |
| *V*, Å$^3$ | 1045.9(9) |
| cell detn, refls | 25 |
| cell detn, $2\theta$ range, deg | 14-18 |
| d(calcd), g cm$^{-3}$ | 2.22 |
| space group | $P2_1/c$ |
| Z | 2 |
| $F_{000}$ | 681.87 |
| radiation | $MoK_\alpha$, graphite monochromated |
| $\lambda$, Å | 0.71073 |
| temp, K | 293 |
| linear abs coeff,mm$^{-1}$ | 2.31 |
| diffractometer | Enraf-Nonius CAD-4 |
| scan technique | $\theta$-$2\theta$ |
| scan speed, deg min$^{-1}$ | 4-16 (in omega) |
| scan width, deg | $1.0 + 0.35\tan\theta$ |
| $2\theta$ range, deg | 4-50 |
| h, k, l ranges | 0,4; 0,11; -36,36 |
| exposure time, hrs | 53.5 |
| std refl indices | 4,0,-8; 0,3,-7; 0,1,11 |
| drift of stds, % | 1.3 |
| absorption correction | empirical psi scans |

| | |
|---|---|
| absorption, range | 0.91-1.00 |
| refl meas | 2154 |
| unique refls | 1823 |
| R for merge | 0.066 |
| data with $I > 3\sigma(I)$ | 1163 |
| solution method | Direct Methods |
| parameters refined | 154 |
| $R(F)$, $R_w(F)$ | 0.047, 0.081 |
| GOF | 1.36 |
| p, $w^{-1} = [\sigma^2(I)+pI^2]/4F^2$ | 0.05 |
| largest $\Delta/\sigma$ | 0.000 |
| extinction correction | none |
| final diff map, e $A^{-3}$ | -0.6(1), +0.5(1) |
| programs | NRC386 (PC version ofNRCVAX)* |
| scattering factors | Internat. Tables for Crystallography Vol 4 |
| H atom treatment | idealized positions (C-H = 0.95Å) |

*PC version of NRCVAX, an interactive program system for structure analysis; see E.J. Gabe, Y. LePage, J.P. Charland, F.L. Lee, and P.S. White, *J. Appl. Cryst.* **22**, 383 (1989).

SPECIAL NOTE: During the refinement of the anisotropic temperature factors of I1 and I2, they were constrained to be equivalent due a large correlation. Iodine position occupancies were determined (I1/I2 = 0.3974/0.3013) during isotropic refinement and locked at those values prior to anisotropic refinement.

**Table S2** Bond distances (Å) and angles (°) for $[P\text{-}2,6\text{-}S]_2[I]$. ESDs refer to the last digit printed.

| Distances | | Angles | |
|---|---|---|---|
| S(1)-S(2) | 2.065(3) | S(2)-S(1)-N(1) | 93.6(3) |
| S(1)-N(1) | 1.607(9) | S(1)-S(2)-N(2) | 95.2(3) |
| S(2)-N(2) | 1.613(8) | S(4)-S(3)-N(3) | 94.2(3) |
| S(3)-S(4) | 2.082(4) | S(3)-S(4)-N(4) | 94.6(3) |
| S(3)-N(3) | 1.629(8) | S(1)-N(1)-C(1) | 117.3(6) |
| S(4)-N(4) | 1.635(8) | S(2)-N(2)-C(1) | 114.7(6) |
| N(1)-C(1) | 1.325(11) | S(3)-N(3)-C(7) | 114.6(6) |
| N(2)-C(1) | 1.358(10) | S(4)-N(4)-C(7) | 113.4(6) |
| N(3)-C(7) | 1.313(12) | C(2)-N(5)-C(6) | 117.6(7) |
| N(4)-C(7) | 1.335(12) | N(1)-C(1)-N(2) | 119.1(7) |
| N(5)-C(2) | 1.351(10) | N(1)-C(1)-C(2) | 119.8(7) |
| N(5)-C(6) | 1.345(11) | N(2)-C(1)-C(2) | 121.0(7) |
| C(1)-C(2) | 1.443(11) | N(5)-C(2)-C(1) | 117.9(7) |
| C(2)-C(3) | 1.393(12) | N(5)-C(2)-C(3) | 121.9(8) |
| C(3)-C(4) | 1.375(13) | C(1)-C(2)-C(3) | 120.2(7) |
| C(4)-C(5) | 1.348(15) | C(2)-C(3)-C(4) | 119.7(8) |
| C(5)-C(6) | 1.382(13) | C(3)-C(4)-C(5) | 117.7(8) |
| C(6)-C(7) | 1.483(13) | C(4)-C(5)-C(6) | 121.6(9) |
| | | N(5)-C(6)-C(5) | 121.4(8) |
| | | N(5)-C(6)-C(7) | 117.5(8) |
| | | C(5)-C(6)-C(7) | 121.1(8) |
| | | N(3)-C(7)-N(4) | 123.3(8) |
| | | N(3)-C(7)-C(6) | 116.5(8) |
| | | N(4)-C(7)-C(6) | 120.1(8) |

**Table S3** Intermolecular S---I contacts (Å) for $[P\text{-}2,6\text{-}S]_2[I]$. ESDs refer to the last digit printed.

| | | |
|---|---|---|
| S3---I1 | (at 1 - x, 0.5 + y, 0.5 - z) | 3.479(3) |
| S3---I2 | (at 2 - x, 0.5 + y, 0.5 - z) | 3.594(7) |
| S3---I2 | (at x - 1, 1.5 - y, 0.5 + z) | 3.428(7) |
| S4---I1 | (at 1 - x, 0.5 + y, 0.5 - z) | 3.748(3) |
| S4---I2 | (at 2 - x, 0.5 + y, 0.5 - z) | 3.842(6) |
| S4---I2 | (at x - 1, 1.5 - y, 0.5 + z) | 3.716(6) |

**Table S4** Anisotropic temperature factors, u(i,j)*100, for $[P\text{-}2,6\text{-}S]_2[I]$. ESDs refer to the last digit printed.

| | u11(U) | u22 | u33 | u12 | u13 | u23 |
|---|---|---|---|---|---|---|
| I1 | 3.2 ( 3) | 3.55( 6) | 3.02( 6) | -0.22(24) | -0.34(21) | -0.22( 4) |
| I2 | 3.2 ( 3) | 3.55( 6) | 3.02( 6) | -0.22(24) | -0.34(21) | -0.22( 4) |
| S1 | 10.8 ( 3) | 2.33(12) | 3.32(13) | 0.60(14) | -2.19(15) | -0.73( 9) |
| S2 | 5.97(17) | 3.16(12) | 2.65(11) | 0.30(12) | -0.79(11) | -0.17( 9) |
| S3 | 8.78(23) | 4.32(14) | 2.79(12) | 2.44(15) | 0.11(14) | -0.50(10) |
| S4 | 6.47(19) | 3.69(14) | 3.74(14) | 1.78(13) | -0.28(13) | -0.22(10) |
| N1 | 5.3 ( 6) | 1.9 ( 3) | 5.7 ( 5) | 0.2 ( 4) | -1.7 ( 4) | -0.1 ( 3) |
| N2 | 3.0 ( 4) | 2.3 ( 3) | 3.6 ( 4) | 0.2 ( 3) | -0.2 ( 3) | -0.2 ( 3) |
| N3 | 5.6 ( 5) | 4.3 ( 4) | 2.8 ( 4) | 1.5 ( 4) | 0.5 ( 4) | 0.4 ( 3) |
| N4 | 6.3 ( 6) | 3.9 ( 4) | 2.1 ( 4) | 1.2 ( 4) | 0.8 ( 4) | 0.2 ( 3) |
| N5 | 1.6 ( 4) | 3.1 ( 4) | 3.4 ( 4) | 0.1 ( 3) | -0.7 ( 3) | 0.3 ( 3) |
| C1 | 4.1 ( 5) | 2.7 ( 4) | 2.0 ( 4) | 0.1 ( 4) | -1.1 ( 4) | 0.2 ( 3) |
| C2 | 1.0 ( 4) | 2.4 ( 4) | 3.7 ( 5) | 0.6 ( 3) | -0.2 ( 4) | 0.3 ( 3) |
| C3 | 2.5 ( 5) | 3.3 ( 5) | 5.6 ( 6) | -0.1 ( 4) | 0.2 ( 5) | 0.8 ( 4) |
| C4 | 2.6 ( 5) | 5.0 ( 6) | 4.1 ( 5) | 0.3 ( 5) | 0.6 ( 4) | 2.0 ( 4) |
| C5 | 2.8 ( 5) | 5.1 ( 6) | 3.6 ( 5) | 0.5 ( 5) | -0.6 ( 4) | 1.8 ( 4) |
| C6 | 2.1 ( 5) | 3.6 ( 5) | 3.2 ( 4) | 1.1 ( 4) | -0.3 ( 4) | -0.1 ( 4) |
| C7 | 3.0 ( 5) | 4.0 ( 5) | 3.5 ( 5) | 1.1 ( 4) | 0.5 ( 4) | 0.1 ( 4) |

Anisotropic temperature factors are of the form:

$$\exp[-2\pi^2(h^2U_{11}a^{*2} + k^2U_{22}b^{*2} + l^2U_{33}c^{*2} + 2hkU_{12}a^*b^* + 2hlU_{13}a^*c^* + 2klU_{23}b^*c^*)].$$

**Figure S1** ORTEP drawing of the asymmetric unit in $[P\text{-}2,6\text{-}S]_2[I]$.